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(54) Title: METHOD FOR BLEACHING OF LIGNOCELLULOSIC FIBERS (57) Abstract The invention relates to a method for the bleaching of lignocellulosic fibers wherein lignocellulosic fibers are treated with at least one oxidizing bleaching chemical in aqueous solution. The invention also relates to the application of additives for bleaching lignocellulosic fibers and to the application of an aqueous solution containing at least one additive for bleaching lignocellulosic fibers. In the context of this paper, the term "lignocellulosic fibers" includes all sorts and types of pulp like e.g. chemical and mechanical pulp, dissolving pulp or pulp prepared from waste paper but also natural fibers like cotton or flax fibers. The method for bleaching of lignocellulosic fibers according to the invention is characterized in that lignocellulosic fibers are treated with at least one oxidizing bleaching agent in aqueous solution in the presence of at least one additive which activates delignification and/or bleaching, the additive being selected among the phenanthrolines and/or polypyridyles. The method is applicable to all known oxidizing bleaching agents like oxygen, ozone and/or peroxo-chemicals or mixtures thereof especially for peroxo-chemicals which comprise hydrogen peroxide, sodium peroxide, perborates, performic acid, peracetic acid or caroic acid and/or salts thereof.		

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METHOD FOR BLEACHING OF LIGNOCELLULOSIC FIBERS

The invention relates to a method for the bleaching of lignocellulosic fibers wherein lignocellulosic fibers are treated with at least one oxidizing bleaching chemical in aqueous solution. The invention also relates to the application of additives for bleaching lignocellulosic fibers and to the application of an aqueous solution containing at least one additive for bleaching lignocellulosic fibers.

In the context of this paper, the term "lignocellulosic fibers" includes all sorts and types of pulp like e.g. chemical and mechanical pulp, dissolving pulp or pulp prepared from waste paper but also natural fibers like cotton or flax fibers.

Pulps produced with alkaline pulping methods, such as the Kraft method, or produced with acid pulping methods such as the acid magnesium bi-sulfite method, or with methods which use organic dissolving agents such as methanol (Organosolv, Organocell, Alcell), or with alkali pulping methods which use, in addition to aqueous alkali, sulfite, anthraquinone and/or other organic solvents such as methanol, e.g. the ASAM method (Alkali-Sulfite-Anthraquinone-Methanol) must be treated in at least one bleaching step after pulping high degrees of brightness.

The state -of- the- art technology for the production of paper or products made from dissolving pulp is based on the use of bleached fibers containing small amounts of residual lignin. An almost completely lignin-free pulp with an α -cellulose content of 98% is required, for example, for dissolving pulps. The fiber must also be free of lignin for chemical pulps as well. The brightness requirements for paper made from recycled fibers are also continually increasing. Fibers primarily used for the production of newspaper such as ground wood, RMP (refiner mechanical pulp), TMP (thermo mechanical pulp), and CTMP (chemo-thermo mechanical pulp) are increasingly being bleached to higher brightnesses, not only with reducing bleaching agents such as hypochlorite (HClO) or dithionite ($\text{SO}_2\text{O}_4^{-2}$) but also

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with oxidizing bleaching agents containing oxygen such as hydrogen peroxide. Because bleaching is no longer conducted exclusively with elemental chlorine or chlorine containing chemicals for environmental and economic reasons, chlorine-free oxidating compounds like oxygen, ozone or peroxo-chemicals like hydrogen peroxide or peracids and mixtures thereof are used more often.

These chlorine-free chemicals comprise mainly oxidizing bleaching chemicals like oxygen, ozone and peroxo-chemicals. Among the peroxo-chemicals, peroxides, especially hydrogen peroxide is well suited to bleach lignocellulosic fibers. However, sodium hydroxide, peracids like peracetic acid, performic acid or Caroic acid and salts thereof are also suited to increase pulp brightness. The increasing trend towards the TCF (total chlorine free) bleaching of all fibrous materials for the production of paper with oxygen, ozone and chemicals containing peroxo compounds necessitates increased efforts to more efficiently utilize and activate these chemicals in the bleaching liquor, thereby attaining higher consumption and higher brightness.

It is very difficult, however, to activate hydrogen peroxide during this procedure by adding more alkali or increasing the temperature. The higher amounts of alkali or the higher temperature can greatly effect the bleaching reaction, leading to a complete consumption of the peroxide in the alkali milieu which results in secondary yellowing. (H. Süss; H. Krüger and K. Schmidt, "Die optimale Bleiche von Holzstoffen und ihre Abwasserbelastung", Papier (34), (10), 1980, pg. 433-438). Thus it has been necessary to retain a certain residual amount of peroxide in the alkali fiber suspension after bleaching to avoid brightness reversion after final bleaching of the fibers.

Peroxide bleaching of fibrous materials used for the production of chemical and dissolving pulps has become a normal practice today. Almost all types of pulps can be bleached at least in single bleaching steps with an alkaline peroxide solution (P stage), often a P-stage is used for brightening the pulp to

final brightness in the final bleaching step. Even during pre-bleaching, delignifying treatment with oxygen (alkaline oxygen stage), increased brightness is attained by adding hydrogen peroxide. Pulps finally bleached with hydrogen peroxide demonstrate however a decreased brightness reversion compared to pulps bleached with a CEDED-sequence by application of elemental chlorine (C), alkaline extractions (E) and chlorine dioxide (D).

For the most part, it is impossible to attain a pulp brightness above 80 % ISO for softwood pulps produced with the alkaline sulfate method (also known as the Kraft method) by TCF bleaching without using ozone and higher dosages of hydrogen peroxide which is not economical. Lab studies have reported on multistage bleaching methods which, with the exclusive use of 7% of hydrogen peroxide, attained a brightness of 88% ISO. These studies are described in ~~the~~ The optimal conditions for P* hydrogen peroxide bleaching~~ing~~ by Desprez, J. J. Devenyns and N. A. Troughten Proc. Pulping Conf. San Diego 929-934 (1994). However, cost of bleaching chemicals is extremely high for this bleaching sequence.

In order to improve the effect of bleaching of peroxo-compounds, efforts have been made to stabilize said peroxo-compounds, i.e. to prevent decomposition of e.g. hydrogen peroxide in the bleaching liquor. Known additives e.g. for stabilizing hydrogen peroxide are sodium silicate, EDTA or DTPA.

Bleaching is usually conducted in several stages. Between these stages the pulp is washed on washing filters. Because of the presence of heavy metal ions in the pulp, which were incorporated into the wood during growth, a chelation should be conducted before peroxide bleaching to reduce catalytic decomposition of peroxide. Chelation is conducted in a separate process step at temperatures between 50 - 90°C and under slightly acidic reaction conditions, e.g. pH level between 4-6 with soluble chelating agents such as EDTA (Ethylene Diamine Tetraacetic Acid) or DTPA (Diethylene Triamine Pentaacetic

Acid), followed by washing. It can also be conducted at acid pH levels between 2-4 with sulfuric acid and at higher temperatures. In the following washing step the acid must be completely removed.

The objective of this invention is to present a method as described in the introduction which allows to make improved use of chlorine-free peroxo-chemicals. This objective is attained according to the invention by treating lignocellulosic fibers with at least one oxidizing bleaching agent in aqueous solution in the presence of at least one additive which activates bleaching; the additive being chosen among the phenanthrolines and/or polypyridyles.

The further objective of this invention is to provide chemicals or mixtures of chemicals suitable for application in pulp bleaching. This objective is attained by providing additives in solid or liquid form for application in bleaching of lignocellulosic fibers.

As outlined above, oxidizing bleaching chemicals are subject to catalytic decomposition. The loss of bleaching chemicals due to catalytic decomposition adds further to the already high cost of chlorine-free oxidizing bleaching chemicals. A first approach to solve this problem was an attempt to remove metal ions by either acid washing or by masking the metal ions by means of chelation. However, decomposition is still very high, especially if hydrogen peroxide is applied. Therefore, it is still aimed to improve stabilizing of oxidative bleaching chemicals. The term "stabilizing" is used in the context of this disclosure if an increase in residual amount of oxidizing bleaching chemical is observed.

However, the present invention does not primarily deal with stabilization of oxidative bleaching chemicals. Instead, it is proposed to enhance the brightening effect of oxidative bleaching chemicals by adding activating additives chosen among the phenanthrolines and/or polypyridyles to the bleaching solution. In the context of this disclosure, "activation"

refers to an additional increase in brightness of the fibers treated under oxidative bleaching conditions.

If the method according to the invention is applied, it is possible to positively activate e.g. the hydrogen peroxide to bleach the lignocellulosic fibrous material to a higher degree of brightness. Through this an exceptional brightness increase is attained, resulting thereby in a greatly improved efficiency of the peroxide bleaching, just by adding an activating additive chosen among the phenanthrolines and/or bipyridyles. Thus the inventive method allows to either reduce the input of oxidative bleaching chemicals or to increase the brightness of the fibers. These positive effects can be observed with additives containing diimine-groups, preferably alpha-alpha-diimine bondings.

Each of these aspects is economically interesting. Reduction of chemical input leads to a reduction of cost of production while increased brightness of fibers allows to demand higher prices for the final product. Besides, the reduction of chemical input implies positive effects with respect to environmental issues. Surprisingly, another advantage of applying activating additives is that they enhance delignification. A reduced content of lignin is closely related to fiber brightness, especially to the degree of final brightness which might be attained after the bleaching process is completed. Thus, the delignifying effect of the activating additives contributes to pulp brightness not only by increasing the efficiency of the oxidizing bleaching chemical but also by supporting pulp delignification.

The invention relates specifically to the application of an activating additive to solutions for bleaching lignocellulosic fibers under oxidizing conditions. Such mixtures improve the efficiency of oxidative bleaching chemicals, especially of peroxo-compounds suitable to bleach lignocellulosic fibrous material to produce chemical or dissolving pulps. This activating additive comprises at least one activating additive

chosen among the phenanthrolines and/or polypyridyles. The positive effects of such mixtures have been described above.

Phenanthrolines and polypyridyles are environmentally feasible compounds. They decompose if the residual bleaching liquor is burnt after bleaching or if the residual bleaching liquor is subjected to biological or chemical wastewater-treatment.

The method according to the invention works for oxidizing bleaching chemicals suited for bleaching of lignocellulosic fibers. It works especially if oxygen, ozone or peroxo-chemicals are applied. Among the peroxo-chemicals, the results achieved in hydrogen peroxide bleaching are very favourable. Here, brightness increase is very high, especially in final bleaching stages. Further, in hydrogen peroxide bleaching (P stages), final brightness is higher than without application of activating additives. However, similar effects can be obtained in sodium peroxide bleaching, in bleaching with perborates, peracetic acid or caroic acids and/or salts thereof like e.g. sodium caroate.

Although application of single additives results in the desired effect of improved brightness of fibers, it is possible to combine two or more of said activating additives to maximize the brightening effect. Surprisingly, repeated use of said activating additives proves to be beneficial. If a bleaching sequence comprises for example two or more P stages, an additional brightening and/or delignifying and/or stabilizing effect will be observed in each peroxide stage. This is astonishing because usually, the effect of additives is exhausted after one application.

Although the activating effect is to be adherent to the phenanthrenes and polypyridyles in general because all of them contain diimine structures, some specific substances proved to be especially effective. These specific substances are

1,10 -phenanthroline (ortho-phenanthroline) and its derivatives, e.g.

1,10 phenanthroline-monohydrate,
1,10 phenanthroline-hydrochloride-hydrate ,
2,9 dimethyl-1,10-phenanthroline,
2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) ,
2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-disulfonic acid
disodium salt hydrate (bathocuproinedisulfonic acid disodium
salt) ,
4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) ,
4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt
hydrate (bathophenanthroline acid disodium salt) ,
5-nitro-1,10-phenanthroline (nitroferroine) ,
4,7-dihydroxy-1,10-phenanthroline,
3,4,7,8-tetra-methyl-1,10-phenanthroline,
4-methylene-1,10-phenanthroline, and
5-methylene-1,10 phenanthroline.

In addition the following substances can be used to activate
the bleaching effect of oxidizing bleaching liquors:

4,5-phenanthroline-monohydrate,
1,7-phenanthroline,
4,7-phenanthroline,
4,7-phenanthroline-5,6 dione,
4,7-phenanthroline-5,6-chinone, and
4,7-phenanthroline-5,6-dion-monoxime.

Among the polypyridyles, bipyridyles proved to be very
efficient. 2,2'-bipyridyl and alpha'-bipyridyl and its
derivatives as well as 2,2'-bipyridylamine are also suited for
the activation of the bleaching effect of peroxide. Other
suitable bipyridyls include:

2,4'-bipyridyle,
3,3'-dihydroxy-2,2'-bipyridyle,
4,4'-bipyridyle and its derivatives, for example
4,4'-bipyridyle-hydrate and
4,4'-bipyridylhydrochloride.

However, also 2,2':6,2'-terpyridine, 2,2':6':2,2'''-tetrapyridine and 2,4,6-tri-2-pyridyle-1,3,5-triazine proved to be suitable for activating oxidizing bleaching chemicals.

Further, N-oxides (nitrogen oxides) and/or metal ion complexes of the aforementioned phenanthrolines and polypyridyles have proven to be especially useful in activating oxidizing bleaching chemicals.

0.001 to 5%
The activating additives are applied at an amount of 0.001 to 5% of additive based on bone dry lignocellulosic fiber. The preferable dosage ranges from 0.01 to 1.0% of additive based on bone dry lignocellulosic fiber. This dosage balances brightness improving effect and additional cost of additive within acceptable limits.

The oxidizing bleaching chemical is applied at an amount of 0.1 to 15% of bleaching chemical based on bone dry lignocellulosic fiber. For economical reasons it is preferred to limit the use of oxidizing bleaching chemicals to 0.5 to 7.0%, even more preferred is a maximum of 5% of bleaching chemical based on bone dry lignocellulosic fiber.

The activating effect of the aforescribed additives does not depend from the pH conditions of the bleaching process. Brightness increase is observed under acidic, neutral and alkaline conditions. However, very favourable results have been achieved within the pH range from 9 to 13.5. The activating additives are not sensitive with respect to the alkali source which is used for pH adjustment. All known alkali sources may be applied, for example sodium hydroxide, magnesium oxide, potassium hydroxide or the like. The alkali dosage ranges preferably from 1.0% to 5.0% based on bone dry fiber.

The activating additives are not sensitive to extreme reaction conditions. Brightness increase of fibers is observed even if bleaching is conducted at high temperatures. Thus, an improved pulp brightness can be achieved if bleaching is carried out within the temperature range of 20 °C to 130 °C. However, it is

preferred to conduct pulp bleaching at temperatures from 40 °C to 80 °C. Reaction may take from 5 to 420 minutes, depending on the specific requirements of the lignocellulosic material to be bleached. It was very unexpected to find that delignification occurred under these mild bleaching conditions. Usually, the structure of residual lignin, especially of Kraft pulps, is described as not accessible due to its high content of condensed components. An additive which is able to render residual lignin accessible for oxidizing agents is thus very much appreciated.

The method according to the invention does not depend on the consistency of the bleaching solution. The content of bone dry lignocellulosic fibers may range from 0.5 to 50% based on water.

The method according to the invention does not depend on the solvent used for bleaching of lignocellulosic fibers. If alcohol is added to the aqueous bleaching solution, the increase of brightness is not affected. The method works even if bleaching is carried out in pure alcoholic solvent. Bleaching in aqueous-alkoholic medium results in improved viscosity of the fibers.

Surprisingly, the activating additives showed a certain stabilizing effect. The residual amount of oxidizing bleaching chemical was higher, if an activating additive was applied. The stabilizing effect is much appreciated because less bleaching chemical is required. Nevertheless, it is considered as an advantage that the activating additives can be applied together with other stabilizing compounds. As outlined above, stabilizing compounds are frequently used to prevent decomposition of oxidizing bleaching chemicals. Often combination of additives of different structure results in counterproductive effects. However, if the method according to the invention is applied, stabilizing compounds may be added without adversely affecting the brightening and/or delignifying effect of the phenanthrolines and/or polypyridyles.

Thus a preferred embodiment of the method according to the invention comprises the joint application of activating additives together with stabilizing compounds. Preferred stabilizing compounds are e.g. poly-alpha-hydroxyacrylic acid, phosphonic acid and its derivatives like e.g. diethylenetriaminopentakis(methylenephosphonic acid) (DTPMPA), or 1-hydroxyethane-1,1-diphosphonic acid, polyaminocarboxylic acid, nitrilotriacetic acid (NTA), salicylic acid, salts of these acids, oxo- or polyoxo-compounds with 2 to 7 carbon atoms in their carbon atom chain, magnesia sulfate or sodium silicate. Further, magnesium ions may be added to the bleaching solution. Any known source of Mg-ions may be used like e.g. magnesium oxide, magnesium heptahydrate or magnesium sulfate. These stabilizing compounds may be applied either singularly or in combination. Especially stabilizing compounds comprising a phosphonic acid component are suited to stabilize oxidizing bleaching agents, like e.g. aminotrimethyl-phosphonic acid (ATMP), ethylenediamine-tetrakis(methylenephosphonic acid) (EDTMPA), triethylenetetraaminhexakis(methylenephosphonic acid) (TTHMP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), 1-hydroxyethane-1,1-diphosphonic acid (HEDP), and/or N-(1-carboxymethyl)-1-amino-ethane-1,1-diphosphonic acid (CADP) as well as their N-oxides and/or their salts, respectively.

An improved method according to the invention comprises the preparation of an aqueous or aqueous-alcoholic mixture of the activating additive or additives and the stabilizing compound or compounds and applying this mixture to the solution of lignocellulosic fibers and oxidizing bleaching chemicals. The positive effect of adding the mixture is not impaired if the mixture is added before, together with or after the bleaching chemical. Adding said mixture reduces handling of fiber bleaching components and allows to make maximum use of the expensive oxidizing bleaching chemicals.

Lignocellulosic fibers treated with oxidizing bleaching chemicals in the presence of an activating additive showed a reduced "yellowing", i.e. a reduced brightness reversion after prolonged exposition to light. This, too, is a commercially

attractive aspect because brightness stability is a parameter of fiber quality and thus an argument in pricing and it enlarges the range of applicability for fiber products.

Phenanthrolines and/or polypyridyles are well suited to activate peroxide due to their stability at higher temperatures and under alkaline and oxidizing conditions.

The advantages which result from the efficient hydrogen peroxide bleaching can be summarized as follows. Bleaching times can be shortened by activating the hydrogen peroxide through the addition of the bleaching activation agents phenanthrolines and/or bipyridyles and/or their derivatives. In addition the use of ecologically questionable and highly poisonous bleaching chemicals such as chlorine, and chemicals containing chlorine such as chlorine dioxide and hypochlorite, is no longer necessary.

The use of the activating additive is explained in the following examples. While the examples indicate preferred reaction conditions, other methods of application are possible and obvious to the expert skilled in the art.

Example 1 Peroxide bleaching (P-stage) of a pre-delignified Kraft spruce pulp

Example 1 demonstrates the considerable improvement of brightness of the bleached pulp and an improved efficiency of the use of hydrogen peroxide obtained when using 1,10-phenanthroline (T6 and T7) or 2,2'-bipyridyl (T8 and T9) as compared to the blind trial T1. In the following, reaction conditions and results are described in detail.

Pre-bleaching

The Kraft spruce pulp was subjected to an alkali/oxygen delignification (O-stage) and an acid washing treatment (A) afterwards. In the alkaline oxygen stage (O), the pulp slurry (10% consistency) was treated for 140 minutes in an electrically heated, rotating, steel autoclave with an aqueous

alkali bleaching liquor, consisting of 2.75% NaOH, and 1.0% MgSO₄, at 110°C and 0.8 MPa. Pressure was adjusted by adding oxygen to the autoclave. In the second treatment step (A-stage), the pulp was adjusted in de-ionized water to a consistency of 3%, and the pH level was reduced to 2 with concentrated sulfuric acid. The pulp was treated for 30 minutes at 70 °C. All of the acid was then washed out of the pulp in a final step. The thus pre-treated pulp was the pulp used in the following peroxide bleaching stage.

The viscosity (T230), the kappa number (T246 and Zellcheming Merkblatt IV/37/63), and the brightness (T217) were determined according to the corresponding test methods of the 'Technical Association of the Pulp and Paper Industry' (TAPPI) or according to the regulations of the Zellcheming pamphlet. After the alkali/oxygen treatment (O) and an acid treatment (A), the pulp had a kappa number of 7.6 and a brightness of 42.3% ISO.

Peroxide bleaching (P)

The chemicals listed in the table 1 were added to the aqueous pulp suspension at a consistency of 10 %. The amount of chemicals was calculated on bone dry (bd) fiber mass.

The alkali pulp suspension was then put in an autoclave lined with polytetrafluorethylene (PTFE) and adjusted to temperature in a silicon oil bath.

At the end of the reaction the residual amount of peroxide in the filtrate of the alkaline bleaching liquor was determined idiometrically in % based on the bd fiber mass. The pulp was washed, and the brightness was determined according to the methods described above. Unless otherwise mentioned, this procedure was maintained for all following examples.

Table 1 presents the parameters and results of T1-T9 of the P-stage.

Table 1

	T1	T2	T3	T4	T5	T6	T7	T8	T9
Temperature (°C)	120	120	120	120	120	120	120	120	120
Time (min)	80	80	80	80	80	80	80	60	60
MgSO ₄	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
NaOH	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
H ₂ O ₂	3.0	3.0	3.0	3.0	3.0	3.0	3.0	4.0	4.0
DTPMP (%)	-	0.01	0.03	0.02	0.05	0.05	0.05	-	-
HEDP (%)	-	0.00 1	0.003	0.002	0.00 5	0.00 5	0.00 5	-	-
Na-Gluconate	-	0.25	0.75	0.50	1.25	1.25	1.25	-	-
1,10-phenanthroline (%)	-	-	-	-	-	0.10	0.20	-	-
2,2'-bipyridyle (%)	-	-	-	-	-	-	-	-	0.2
H ₂ O ₂ at end of reaction (%)	0.17	0.77	0.77	0.82	1.36	1.22	1.00	1.72	0.22
Kappa number (-)	-	-	-	-	-	-	-	4.8	3.1
Brightness (% ISO)	71.3	71.9	75.0	73.6	74.5	81.2	82.5	75.8	83.5

T1 shows the effect of hydrogen peroxide bleaching without adding additives. Brightness increases from initially 42.3 % ISO to 71.3 % ISO. If stabilizing agents are applied (T2 to T5), brightness increases further by another 0.6 to 3.2 %ISO. Application of 0.1 % or 0.2 % activating additive (1,10-phenanthroline) causes another increase in brightness from 71.3 %ISO to 81.2 % ISO and 82.5 % ISO, respectively; see T6 and T7. However, the increase in brightness does not depend on the presence of stabilizing agents. T8 and T9 show that the application of 4% hydrogen peroxide alone results in a brightness of 75.8 %ISO. If 0.2 % of activating additive (2,2'-bipyridyl) is applied, brightness increases by another 7.8 %ISO and the residual lignin content is reduced by 1.5 Kappa numbers. While the application of 0.2 % of activating additive leads to an increase in brightness of 11.2 % ISO (T1/T7) and

7.8 %ISO (T8/T9), an increase of the amount of hydrogen peroxide from 3% to 4% based on bd pulp allows an increase in brightness of 4.5 %ISO only.

Example 2 Oxygen-peroxide bleaching (OP) of a pre-delignified Kraft spruce pulp

In Example 2 the brightness increase of the pulp bleached in an OP bleaching step with the addition of 1,10-phenanthroline (T11-T13) is compared to the blind trial (T10).

Pretreatment

The treatment and properties of the pulp are the same as described in Example 1.

Oxygen Peroxide bleaching (OP)

The chemicals listed in the table were added to the aqueous pulp suspension based on the bd fiber mass at a consistency of 10%. The alkali pulp suspension was then put in an autoclave lined with polytetrafluorethyl (PTFE) and adjusted to temperature in a silicon oil bath.

At the end of the reaction the residual amount of peroxide in the filtrate of the alkali bleaching liquor was iodometrically determined based on the bd fiber mass. The pulp was washed, and the brightness was determined according to the methods described above.

Table 2 presents the parameters and results of T10-T13 of the OP-stage.

Table 2

	T10	T11	T12	T13
Temperature (°C)	120	120	120	120
Time (min)	80	80	80	80
MgSO ₄	0.5	0.5	0.5	0.5
NaOH	1.5	1.5	1.5	1.5
H ₂ O ₂	4.0	4.0	4.0	4.0
DTPMP (%)	0.03	0.03	0.03	0.03
HEDP (%)	0.003	0.003	0.003	0.003
Na-Gluconate	0.75	0.75	0.75	0.75
1,10-phenanthroline (%)	-	0.10	0.15	0.20
H ₂ O ₂ at end of reaction (%)	1.40	1.00	0.80	0.60
Kappa number (-)	3.5	2.7	2.7	2.5
Brightness (% ISO)	80.5	86.3	87.6	88.1

The addition of the activating additive not only caused an increase in brightness by 8 %ISO but also reduced the residual lignin content. Addition of 1,10-phenanthroline improved the pulp brightness although the overall brightness level of the pulp is already high. The reduction of residual lignin content is especially remarkable because reaction conditions are quite mild compared to pulping conditions.

Example 3 Peroxide bleaching (P) of an OA (OP) pretreated Kraft spruce pulp

Example 3 demonstrates that, even with a smaller dosage of 1,10-phenanthroline and a lower bleaching temperature than in the preceding examples, it is possible to obtain greater brightness increases than in the blind trial T14 (T15-T19).

Pre-treatment

The alkali/oxygen treatment (O) and the acid pre-treatment (A) correspond to the treatment described in Example 1. The

following oxygen/peroxide bleaching was also conducted in an electrically heated rotating steel autoclave at 100°C and at an oxygen pressure of 0.8 MPa. 2.0% NaOH, 1.0% MgSO₄, 0.66% nitrilamine, and 2.0% H₂O₂ were added to the aqueous fibrous suspension. Bleaching time was 140 min.

After the OA (OP) pre-bleaching, the brightness of the pulp was 73.6%, the kappa number 2.6, and viscosity 761 ml/g.

Peroxide bleaching

The following peroxide bleaching was conducted in polyethylene bags, which were adjusted to temperature in a water bath. The consistency was 10%. The chemicals added to the pulp are listed in Table 3.

At the end of the reaction the residual amount of peroxide in the filtrate of the alkali bleaching liquor was idiometrically determined based on the bd fiber mass. The pulp was washed, and the brightness was determined according to the methods described above.

Table 3 presents the parameters and results of T14-T19 of the P-stage following the pre-treatment.

Table 3

	T14	T15	T16	T17	T18	T19
Temperature (°C)	90	90	90	90	90	90
Time (min)	240	240	240	240	240	240
MgSO ₄	0.5	0.5	0.5	0.5	0.5	0.5
NaOH	1.5	1.5	1.5	1.5	1.5	1.5
H ₂ O ₂	2.0	2.0	2.0	2.0	2.0	2.0
1,10-phenanthroline (%)	-	0.012 5	0.025	0.05	0.10	0.20
H ₂ O ₂ at end of reaction time (%)	1.28	1.17	1.14	1.11	0.99	0.71
Brightness (%ISO)	77.3	79.3	80.4	81.3	82.3	82.9

A 2 %ISO higher brightness can be obtained with just 0.0125% of additive based on the bd fiber mass. The use of 0.2% of the activating additive led to a brightness increase of approximately 6%ISO. The continuous increase in brightness indicates that a further increase in pulp brightness may be achieved by adding more activating additive. However, in order to limit cost of bleaching, the application of additive was restricted to 0.2% based on bd lignocellulosic fiber. If the price of the activating additive goes down, a higher dose of additive will allow to increase final pulp brightness further.

Example 4 Oxygen/peroxide treatment (OP) of an unbleached, untreated Kraft spruce pulp

In Example 4 it is demonstrated how the use of an additive lowers the lignin content of the pulp (T21) compared to a blind trial without the additive (T20). Kappa number after pulping and prior to oxygen delignification was determined to be 22.3.

Without any pre-treatment, the Kraft spruce pulp was bleached at a consistency of 10% and at 0.8 MPa pressure in an initial OP bleaching step in autoclaves rotated in a silicon bath heated to reaction temperature. Pressure was adjusted by adding oxygen. The chemicals listed in Table 4 were added to the pulp beforehand. The pulp was washed, and the brightness was determined according to the methods described above. In Table 4 the parameters and results of T20 and T 21 are compared.

Table 4

	T20	T21
Temperature (°C)	120	120
Time (min)	60	60
MgSO ₄	1.0	1.0
NaOH	2.75	2.75
H ₂ O ₂	2.0	2.0
1,10-phenanthroline (%)	-	0.20
Kappa number (-)	14.2	13.1

Example 5 Oxygen/peroxide bleaching (OP) of a pretreated Kraft hardwood pulp (eucalyptus)

In Example 5 the treatment according to the invention also demonstrates a positive effect during the bleaching of the Kraft eucalyptus pulp.

The eucalyptus pulp, industrially pre-treated by an alkali-oxygen delignification to a kappa number of 7.9, with a viscosity of 848 ml/g and a brightness of 40% ISO, was bleached further in an oxygen/peroxide bleaching step. Pressure was adjusted to 0.8 MPa by adding oxygen. The parameters and results of the (OP) bleaching are listed in Table 5.

Table 5

	T22	T23
Temperature (°C)	100	100
Time (min)	60	60
MgSO ₄	0.5	0.5
NaOH	1.5	1.5
H ₂ O ₂	4.0	4.0
1,10-phenanthroline (%)	-	0.10
Brightness (%ISO)	71.6	78.7
H ₂ O ₂ at end of reaction (%)	1.46	1.57

The chemicals listed in Table 5 were added to the aqueous fibrous suspension at 10% consistency based on the bd fiber mass. The fibrous suspension was then put into an autoclave lined with polytetrafluorethylene (PTFE) under 0.8 MPa and adjusted to temperature in a rotating silicon oil bath. At the end of the reaction the residual amount of peroxide in the filtrate of the alkaline bleaching liquor was idiometrically determined based on the bd fiber mass. The pulp was washed, and the brightness was determined according to the methods described above.

Compared to Example 1, the activating additive proves to be even more efficient in bleaching hardwood pulp. Here, the stabilizing effect of 1,10-phenanthroline becomes apparent. Although brightness increased by 7.1 %ISO, residual peroxide content increased, too.

Example 6 Bleaching of waste paper

In Example 6 the inventive method was also used to bleach a de-inked 70/30 (magazine/ newspaper) mixture of waste paper pulp and also obtained very positive results.

The waste paper was only de-inked before bleaching. Neither chelation nor any other kind of pretreatment was conducted. In Table 6 the parameters and results of T 24 and T25 are compared.

Table 6

	T24	T25
Temperature (°C)	90	90
Time (min)	180	180
MgSO ₄	0.5	0.5
NaOH	2	1.5
H ₂ O ₂	5.0	5.0
Sodium silicate (%)	1.5	1.5
DTPA (%)	0.3	0.3
1,10-phenanthroline (%)	-	0.10
Brightness (%ISO)	71.3	72.8
H ₂ O ₂ at end of reaction (%)	0.19	1.79

Even after de-inking, waste paper pulp contains an extremely high amount of impurities like ink, clay, resins and other material used in paper production and printing. Because hydrogen peroxide is highly sensitive to these compounds,

decomposition is high and the brightening effect is very much limited. Although stabilizing compounds (Sodium silicate, DTPA) were added in the blind trial, too, addition of 1,10-phenanthroline proved not only to be efficient in increasing fiber brightness but also to prevent decomposition of hydrogen peroxide. The stabilizing effect of phenanthroline appears to be different from the reaction mechanism of the other stabilizing compounds and phenanthroline thus acts synergistic.

Example 7 Oxygen/peroxide bleaching (OP) of an unbleached ASAM pine pulp

In example 7 the method according to the invention is used to bleach a pine pulp cooked according to an alkali pulping method with anthraquinone and methanol known as ASAM.

Usually, bleaching is conducted in aqueous solutions. But also mixtures of water and alcohol, for example ethanol, methanol or butanol can be used as solvent. Bleaching in pure alcohol is possible, too. The additive acts as an activator and leads to an increase in pulp brightness. The results of Ta, Tb, Tc and Td indicate that addition of alcohol does not impair the effect of the activating additive. Viscosity of fibers bleached with the activating additive is higher than compared to the blind trial. This holds true for bleaching in aqueous solution as well as in aqueous-alcoholic solution. It is surprising that the activating additive causes an increase in pulp brightness although the amount of alkali is rather high.

The conditions and results of the trials are listed in Table 7.

Table 7

	T26	T27	Ta	Tb	Tc	Td
Temperature [°C]	120	120	120	120	120	120
Time [min]	90	90	90	90	90	90
MgSO ₄ [%]	0,25	0,25	0,35	0,35	0,35	0,35
NaOH [%]	3,5	3,5	3,5	3,5	3,5	3,5
H ₂ O ₂ [%]	5,0	5,0	5,0	5,0	5,0	5,0
Methanol [%]	-	-	-	-	0,1	0,1
Poly-a-hydroxiacrylic acid [%]	0,1	0,1	0,1	0,1	0,1	0,1
1,10-phenanthroline [%]	-	0,1	-	0,1	-	0,1
H ₂ O ₂ at end of reaction [%]	12,2	9,5	17,7	13,3	16,0	7,5
Brightness [% ISO]	82,5	84,5	83,5	85,2	83,6	85,2
Viscosity [ml/g]	964	795	946	798	1063	893

Example 8 OP-Bleaching of a pretreated Kraft spruce pulp

The pulp bleached in Example 8 was pretreated like the pulp used in Example 1. The pulp had a Kappa number of 7.5 and a brightness of 42.3 %ISO prior to the OP bleaching stage. Table 8 shows reaction conditions and results of the OP bleaching stage.

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline does not only lead to a considerable increase in pulp brightness but shows also a high ability to stabilize hydrogen peroxide. Brightness increase is almost as high as with 1,10-phenanthroline but peroxide stabilization is much improved compared to 1,10-phenanthroline. 5-nitro-1,10-phenanthroline improves pulp brightness although the increase in pulp brightness is not as high as for the other additives.

Table 8

	T28	T29	T30	T31	T32	T33	T34
Temperature [°C]	120	120	120	120	120	120	120
Time [min]	60	60	60	60	60	60	60
MgSO ₄ [%]	0,5	0,5	0,5	0,5	0,5	0,5	0,5
NaOH [%]	1,5	1,5	1,5	1,5	1,5	1,5	1,5
H ₂ O ₂ [%]	4	4	4	4	4	4	4
2,9-dimethylene- 4,7-diphenyl- 1,10-phenanthroline [%]	-	0,25	-	-	-	-	-
5-Nitro-1,10- phenanthroline [%]	-	-	0,25	0,5	-	-	-
1,10-phenanthroline [%]	-	-	-	-	0,25	-	-
phenanthrenchinone [%]	-	-	-	-	-	0,5	1,0
Brightness [%ISO]	75,6	79,8	77,0	77,2	80,5	76,4	75,4
H ₂ O ₂ at end of reaction [%]	29,9	50,2	27,6	21,7	24,2	30,2	30,9

**Example 9 Hydrogen peroxide bleaching of a Kraft spruce
pulp prebleached with ozone (Z stage)**

The pulp bleached in Example 9 originated from an industry sample and showed the following properties prior to peroxide bleaching: Kappa number 1.8; pulp viscosity 542 ml/g; brightness: 75.7 %ISO.

Table 9 shows reaction conditions and results of peroxide bleaching.

Application of 4-methyl-1,10-phenanthroline causes an activation of hydrogen peroxide which is even more efficient than the activation effect of 1,10-phenanthroline. While the blind trial (T35) results in a brightness of 84.8 %ISO,

application of small amounts of 4-methyl-1,10-phenanthroline result in a final pulp brightness of 87.9 %ISO at best. Small amounts of 1,10-phenanthroline allow a final brightness of 86,5 %ISO. Results achieved with only minor amounts of activating additives showed a significant increase in brightness which could not be anticipated.

Table 9

	T35	T36	T37	T38	T39	T40	T41	T42	T43
Temperature [°C]	90	90	90	90	90	90	90	90	90
Time [min]	90	90	90	90	90	90	90	90	90
MgSO ₄ [%]	-	-	-	-	-	-	-	-	-
NaOH [%]	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5
H ₂ O ₂ [%]	2	2	2	2	2	2	2	2	2
4-methylene-1,10-phenanthroline [%]	-	0,0 25	0,0 5	0,0 75	0,1	-	-	-	-
1,10-phenanthroline [%]	-	-	-	-	-	0,0 25	0,0 5	0,0 75	0,1
Brightness [%ISO]	84, 8	86, 7	86, 9	87, 5	87, 9	86, 6	86, 4	86, 4	86, 5
H ₂ O ₂ at end of reaction [%]	94, 4	88, 4	87, 6	83, 3	79, 1	91, 0	89, 3	86, 0	84, 2

Example 10 Peroxide bleaching of an oxygen pretreated Kraft spruce pulp

The kraft spruce pulp was pretreated like the pulp described in Example 1. After oxygen pretreatment, a chelating treatment followed (Q stage). Chelation was carried out at 3% consistency and 60 °C for 60 minutes. 0.5% DTPA were applied as chelating agent.

Prior to peroxide bleaching, the pulp showed a Kappa number of 8.0; viscosity: 807 ml/g; brightness: 40.4 %ISO.

Table 10/1 and 10/2

	T44	T45	T46	T47	T48	T49	T50	T51	T52
Temperature [°C]	120	120	120	120	120	120	120	120	120
Time [min]	90	90	90	90	90	90	90	90	90
MgSO ₄ [%]	-	-	-	-	-	-	-	-	-
NaOH [%]	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5
H ₂ O ₂ [%]	4	4	4	4	4	4	4	4	4
3,4,7,8-tetramethylene-1,10-phenanthroline [%]	-	0,0 25	0,0 5	0,1	0,1 5	-	-	-	-
1,10-phenanthroline [%]	-	-	-	-	-	0,0 25	0,0 5	0,1	0,1 5
2,2'-bipyridyle	-	-	-	-	-	-	-	-	-
Brightness [%ISO]	76, 5	79, 3	80, 7	81, 1	81, 7	78, 9	80, 2	81, 1	81, 4
H ₂ O ₂ at end of reaction [%]	17, 0	25, 1	22, 5	21, 7	19, 1	19, 6	20, 4	17, 9	14, 5
Viscosity [ml/g]	641	624	601	578	546	599	581	554	514

Table 10/1

Addition of even smallest amounts of activating additives (0.025 % based on bone dry fiber) leads to an increase in pulp brightness. Especially 3,4,7,8-tetramethyl-1,10-phenanthroline proves to be efficient although the brightness level of the pulp is already high. Besides its brightening effect, this additive causes a significantly reduced loss in viscosity. A reduced decrease of viscosity usually implies an increased yield because less carbohydrates have been solubilized during bleaching. Further, strength properties correlate positively with pulp viscosity. High viscosity usually indicates high pulp strength.

	T53	T54	T55	T56
Temperature [°C]	120	120	120	120
Time [min]	90	90	90	90
MgSO ₄ [%]	-	-	-	-
NaOH [%]	1,5	1,5	1,5	1,5
H ₂ O ₂ [%]	4	4	4	4
3,4,7,8-tetramethylene-1,10-phenanthroline [%]	-	-	-	-
1,10-phenanthroline [%]	-	-	-	-
2,2'-bipyridyle	0,0 25	0,0 5	0,1	0,1 5
Brightness [%ISO]	77, 7	79, 3	80, 0	80, 5
H ₂ O ₂ at end of reaction [%]	16, 2	12, 8	7,7	6,4
Viscosity [ml/g]	576	550	510	489

Table 10/2

Example 11 Peroxide bleaching of a pretreated Kraft spruce pulp

The Kraft spruce pulp and the pretreatment conditions are the same as described in Example 10. Table 11 shows reaction conditions and results of peroxide bleaching.

Example 11 shows the very favorable effect of 4-methyl-1,10-phenanthroline compared to 1,10-phenanthroline. Even smallest amounts of 4-methyl-1,10-phenanthroline lead to considerably increased pulp brightness. When increasing the amount of additive from 0.025 % to 0.15 % based on bd lignocellulosic fiber, no slowing down of brightness increase can be found. Even under the mild conditions of peroxide bleaching (low temperatures), the additive causes further delignification of the pulp. Delignification, too is more efficient than with 1,10-phenanthroline although here, too, residual lignin content

is reduced significantly. At the same time pulp viscosity is much less affected with 4-methyl-1,10-phenanthroline. The combined effect of brightening, delignification and protection of viscosity was an unexpected achievement and will contribute considerably to improve fiber quality.

Table 11

	T57	T58	T59	T60	T61	T62	T63	T64	T65
Temperature [°C]	90	90	90	90	90	90	90	90	90
Time [min]	180	180	180	180	180	180	180	180	180
MgSO ₄ [%]	-	-	-	-	-	-	-	-	-
NaOH [%]	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5
H ₂ O ₂ [%]	4	4	4	4	4	4	4	4	4
4-methylene-1,10-phenanthroline [%]	-	0,0 25	0,0 5	0,1	0,1 5	-	-	-	-
1,10-phenanthroline [%]	-	-	-	-	-	0,0 25	0,0 5	0,1	0,1 5
Brightness [%ISO]	69, 6	80, 5	82, 4	81, 0	85, 2	75, 1	77, 1	78, 1	79, 0
H ₂ O ₂ at end of reaction [%]	44, 2	11, 9	13, 6	2,1	2,1	25, 1	22, 5	19, 1	15, 7
Viscosity [ml/g]	737	672	636	573	538	659	633	591	555
Kappa number [-]	5,1	4,3	4,0	3,7	3,5	4,6	4,3	4,1	3,9

Example 12 Repeated use of activating additive

In Example 12, a spruce Kraft pulp was bleached with a total chlorine free bleaching sequence. Following an oxygen delignification and a chelation treatment, an oxygen-hydrogen peroxide (OP) stage was conducted. Reaction time was either 240 min (T 66; OQ(OP)1) or 300 minutes (T69; OQ(OP)2). The (OP) stage was conducted in the presence of an activating additive, i.e. 1,10-phenanthroline (phen = 0.05%). Final peroxide bleaching (P) was conducted without activating additive (T67, T68; T70, T71) or with activating additive (T72, T73). Further, the effect of a stabilizing compound was tested (T74, T75; NTA =

nitritotriamine acid). Surprisingly, the addition of an activating additive (T72, T73) led to an improved final brightness of the pulp although the same activating additive had already been used in the same bleaching sequence in an earlier stage. Even minor amounts (0.025% based on bd pulp) show a significant increase of brightness. Addition of NTA neither improved brightness nor delignification. However, residual hydrogen peroxide content of the bleaching solution was improved.

Table 12

Bleaching sequence	No. of trial	time [min]	Temp. [°C]	H ₂ O ₂ [%]	NaOH [%]	MgSO ₄ [%]	phen [%]	NTA [%]	pH start	pH end	residual H ₂ O ₂ [%]	Kappa number [-]	Bright-ness [%ISO]	Viscosity [ml/g]
OQ(OP)	T 66	240	90	3,0	2,0	0,1	0,05	-	11,3	11,2	44,2	3,5	83,5	643
OQ(OP) 1 P	T 67	180	90	1,0	1,5	0,1	-	-	11,7	11,5	35,7	2,8	86,0	620
OQ(OP) 1 P	T 68	180	90	2,0	1,5	0,1	-	-	11,7	11,6	62,9	2,7	87,2	595
OQ(OP)	T 69	300	90	3,0	2,0	0,1	0,05	-	11,3	11,0	43,0	3,4	85,0	625
OQ(OP) 2 P	T 70	180	90	1,0	1,5	0,1	-	-	11,7	11,5	34,0	2,7	86,2	590
OQ(OP) 2 P	T 71	180	90	2,0	1,5	0,1	-	-	11,7	11,6	45,9	2,6	87,5	553
OQ(OP) 2 P	T 72	180	90	1,0	1,5	0,1	0,025	-	11,7	11,6	23,8	2,6	87,8	552
OQ(OP) 2 P	T 73	180	90	2,0	1,5	0,1	0,025	-	11,7	11,5	41,7	2,6	88,3	533
OQ(OP) 2 P	T 74	180	90	2,0	1,5	0,1	-	0,1	11,7	11,6	45,9	2,6	87,7	557
OQ(OP) 2 P	T 75	180	90	2,0	1,5	0,1	-	0,3	11,7	11,6	62,0	2,7	87,0	591

5g bd fibers per batch , consistency: 10% , pressure: 0,8 MPa O₂ phen = 1,10-phenanthroline
 V 66/ OQ parameters of spruce Kraft pulp after oxygen delignification and chelation, but prior to bleaching:

Kappa no. 8,2 ; Viscosity: 825ml/g ; Brightness: 45,1% ISO

O = oxygen stage; Q = chelation; (OP) = oxygen stage with addition of hydrogen peroxide
 residual hydrogen peroxide content here is calculated on 100% hydrogen peroxide input

Claims

1. Method for bleaching of lignocellulosic fibers wherein lignocellulosic fibers are treated with at least one oxidizing bleaching agent in aqueous solution in the presence of at least one additive which activates delignification and/or bleaching, the additive being selected among the phenanthrolines and/or polypyridyles.
2. Method for bleaching of lignocellulosic fibers according to claim 1, characterized in that the oxidizing bleaching agent is oxygen, ozone and/or peroxo-chemicals or mixtures thereof.
3. Method for bleaching of lignocellulosic fibers according to claim 1 or 2, characterized in that the peroxo-chemicals are hydrogen peroxide, sodium peroxide, perborates, performic acid, peracetic acid or carboxylic acid and/or salts thereof.
4. Method for bleaching of lignocellulosic fibers according to at least one of the preceding claims, characterized in that at least one of the activating additives listed hereinafter is used:

among the phenanthrolines:

- 1,10-phenanthroline (ortho-phenanthroline) and/or its N-oxide and/or its metal complexes
- 1,10-phenanthroline monohydrate and/or its N-oxide and/or its metal complexes
- 1,10-phenanthroline hydrochloride hydrate and/or its N-oxide and/or its metal complexes
- 2,9-dimethyl-1, 10-phenanthroline and/or its N-oxide and/or its metal complexes
- 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) and/or its N-oxide and/or its metal complexes
- 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-disulfonic acid-di-sodium salt-hydrate (bathocuproindisulfonic acid

disodium salt) and/or its N-oxide and/or its metal complexes

- 4,7-dimethyl-1,10-phenanthroline (bathophenanthroline) and/or its N-oxide and/or its metal complexes
- 4,7-diphenyl-1,10-phenanthroline-disulfonic acid-disodium salt hydrate (bathophenanthroline disulfonic acid disodium salt hydrate) and/or its N-oxide and/or its metal complexes
- 5-nitro-1, 10-phenanthroline (nitroferrine) and/or its N-oxide and/or its metal complexes
- 4,7-dihydroxy-1, 10-phenanthroline and/or its N-oxide and/or its metal complexes
- 3,4,7,8-tetramethyl-1, 10-phenanthroline and/or its N-oxide and/or its metal complexes
- 4-methylene-1, 10-phenanthroline and/or its N-oxide and/or its metal complexes
- 5-methylene-1, 10-phenanthroline and/or its N-oxide and/or its metal complexes
- 4,5-phenanthroline monohydrate and/or its N-oxide and/or its metal complexes
- 1,7-phenanthroline and/or its N-oxide and/or its metal complexes
- 4,7-phenanthroline and/or its N-oxide and/or its metal complexes
- 4,7-phenanthroline-5,6 dione and/or its N-oxide and/or its metal complexes
- 4,7-phenanthroline-5,6 chinone and/or its N-oxide and/or its metal complexes
- 4,7-phenanthroline-5,6-dione-monoxime and/or its N-oxide and/or its metal complexes

among the polypyridyls

- 2,2-bipyridyl (alpha, alpha'-bipyridyl) and/or its N-oxide and/or its metal complexes
- 2,2-bipyridylamine and/or its N-oxide and/or its metal complexes
- 2,4-bipyridyl and/or its N-oxide and/or its metal complexes

- 3,3-dihydroxy-2,2'-bipyridyl and/or its N-oxide and/or its metal complexes
 - 4,4'-bipyridyl and/or its N-oxide and/or its metal complexes
 - 4,4'-bipyridyl hydrate and/or its N-oxide and/or its metal complexes
 - 4,4'-bipyridyl dihydrochloride and/or its N-oxide and/or its metal complexes
 - 2,2': 6,2'-terpyridine and/or its N-oxide and/or its metal complexes
 - 2,2': 6': 2,2'-tetrapyridine and/or its N-oxide and/or its metal complexes or
 - 2,4,6-tri-2-pyridyl-1,2,5-triazine and/or its N-oxide and/or its metal complexes.
5. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that a mixture of at least two activating additives is applied.
6. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that the amount of activating additives ranges from 0.001 to 5.0% of additive based on bone dry lignocellulosic fibers.
7. Method for bleaching lignocellulosic fibers according to claim 6, characterized in that the amount of activating additives ranges from 0.01 to 1.0% of additive based on bone dry lignocellulosic fibers.
8. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that the amount of oxidizing bleaching agent ranges from 0.1 to 15.0% of bleaching chemical based on bone dry lignocellulosic fibers.
9. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that bleaching is conducted under acidic, neutral or alkaline conditions.

10. Method for bleaching lignocellulosic fibers according to claim 9, characterized in that the pH ranges from 8 to 13.5.
11. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that consistency of the solution ranges from 0.5 to 50% of bone dry lignocellulosic fiber based on water.
12. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that the temperature during treatment ranges from 20 °C to 130 °C.
13. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that the time of treatment ranges from 5 to 420 minutes.
14. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that alcohol is added to the solution.
15. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that at least one stabilizing compound is added to the solution.
16. Method for bleaching lignocellulosic fibers according to claim 15, characterized in that the stabilizing compound is one chosen among poly-alpha-hydroxyacrylic acid, phosphonic acid and/or its derivatives, polyaminocarboxylic acid, nitrilotriacetic acid(NTA), salicylic acid, salts of these acids, oxi- or polyoxi-compounds with 2 to 7 carbon atoms in their carbon atom chain, magnesium compounds and/or sodium silicate.
17. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that the activating additive and the stabilizing compound are mixed as an aqueous or aqueous-alcoholic mixture and that

this mixture is added to the solution of lignocellulosic fibers, water and bleaching chemical.

18. Method for bleaching lignocellulosic fibers according to the preceding claim, characterized in that the mixture of activating additive and stabilizing compound is added prior, after or together with applying the bleaching chemical.
19. Method for bleaching lignocellulosic fibers according to at least one of the preceding claims, characterized in that the activating additive is applied in at least two separate stages of the bleaching sequence.
20. Application of at least one activating additive selected from the phenanthrolines and/or the polypyridyles , preferably selected from the activating additives as described in claim 4 for the bleaching of lignocellulosic fibers.
21. Application of at least one activating additive for the bleaching of lignocellulosic fibers.
22. Application of an aqueous solution of at least one activating additive selected from the phenanthrolines and/or the polypyridyles , preferably selected from the activating additives as described in claim 4 for the bleaching of lignocellulosic fibers.
23. Application of an aqueous solution of at least one activating additive selected from the phenanthrolines and/or the polypyridyles, preferably selected from the activating additives as described in claim 4 and at least one stabilizing compound, especially a stabilizing compound selected from the compounds listed in claims 16 to 23 for the bleaching of lignocellulosic fibers.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/01865

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21C9/10 D21C9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9615 Derwent Publications Ltd., London, GB; Class F09, AN 96-149880 XP002039786 & RU 2 040 617 C (AS SIBE IRKUT ORGANIC CHEM) , 27 July 1995 see abstract ---	1-4,6,7, 9,20-22
X	US 3 736 224 A (GRAYSON M ET AL) 29 May 1973 see column 2, line 25; claims; example 4 --- -/--	1,2,4,6, 7,9-13, 20-22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 September 1997

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30.09.97

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/01865

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PATENT ABSTRACTS OF JAPAN vol. 095, no. 001, 28 February 1995 & JP 06 293900 A (LION CORP), 21 October 1994, see abstract & DATABASE WPI Section Ch, Week 9502 Derwent Publications Ltd., London, GB; Class A97, AN 95-009705 & JP 06 293 900 (LION CORP) , 21 October 1994 see abstract</p> <p style="text-align: center;">---</p>	1-6,15, 16,20-23
X	<p>DATABASE PAPERCHEM THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US AA-AB6508784, BABKIN, V. A. ET AL: "Chlorine-Free Bleaching of Kraft Hardwood Cellulose [Pulp]" XP002039785 & 1994 INTERNATIONAL PULP BLEACHING CONFERENCE: TEXT OF POSTERS TO BE PRESENTED WEDNESDAY, JUNE 15, 1994 (CPPA, TAPPI, SVENSKA PAPERS, AND COMITE EUROPEEN DE LIAISON POUR LA CELLULOSE ET LE PAPIER): 199-203 (JUNE 15, 1994;CPPA). [ENGL.], see page 200, left-hand column</p> <p style="text-align: center;">---</p>	1-4, 6-13, 20-23
P,X	<p>WOCHENBLATT FÜR PAPIERFABRIKATION, vol. 124, no. 17, 15 September 1996, GERMANY, pages 750-755, XP002039784 PATT, R., JASCHINSKI, T.; MIELISCH, J.: "Stabilisierte und katalysierte Peroxidbleiche" see page 754, right-hand column - page 755</p> <p style="text-align: center;">-----</p>	1-3, 6-13,15, 16,20-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/01865

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3736224 A	29-05-73	NONE	
